

10/538891

- 1. -

ANTIOXIDANT FOR FATS, OILS AND FOOD

Background of the Invention

5 The invention relates to the stabilization of edible organic substances subject to deterioration by oxidation. Antioxidants are of great importance in edible fats and fatty oils such as fatty acid glycerides, and in foods made with edible fats and fatty oils. The antioxidants are used to prevent or alleviate oxidative rancidity which causes undesirable flavors and odors, destroys fat-soluble vitamins and essential fatty acids, and produces toxicological effects. A food antioxidant should not impart undesirable characteristics, such as unpleasant odor or discoloration and advantageously has good carry-through which is the ability to survive baking or frying operations and provide improved keeping quality in food prepared from the stabilized edible organic substances.

15 The art shows many methods of inhibiting lipid oxidation by adding fat-soluble antioxidants to the substrate. The art does not show the stabilization of fats, oils, fatty foods and ingredients of foods employing one or more antioxidants selected from the group consisting of 3-arylbenzofuranones, long chain N,N-dialkylhydroxylamines, substituted hydroxylamines, nitrones, and amine oxides as defined hereinafter.

20 Phenols are commonly employed as antioxidants to stabilize organic materials and substituted phenols have been found to have improved antioxidant effectiveness since the efficiency of the phenol group in terminating oxidation is affected by the nature of the ring substituents. Some known phenolic antioxidants are not suitable for use in food because they are toxic to higher forms of animal life. For example, p-aminophenol is highly toxic and is a skin irritant.

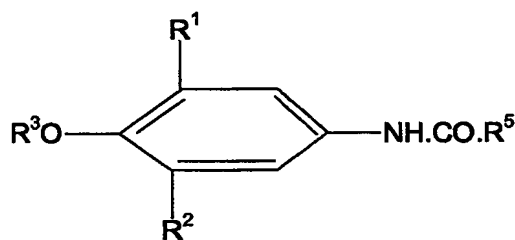
25 Several phenolics have been used as antioxidants in foodstuffs, including butylated hydroxytoluene (BHT) and butylated hydroxyanisole (BHA). Even these antioxidants are now being examined by regulatory agencies and consumer activists and these developments have urged the need to exploit new sources of antioxidants for use in food applications. Also propyl gallate (PG), t-butylhydroxyquinone (TBHQ), iso-ascorbic acid, chloro-iso-ascorbic acid and ascorbyl palmitate have been permitted for use in food applications.

- 2 -

Young, U.S. Patent No. 2,654,722, discloses the use of acyl-p-aminophenols to stabilize solid organic materials, such as synthetic rubbers, which tend to deteriorate due to oxidation. The acyl substituent in these antioxidants has at least three carbon atoms and can be employed as food stabilizers.

5

U.S. Patent No. 3,492,349 to Doyle and Baxter discloses di-lower alkyl-alkoxy- and hydroxyacetanilides. The patent teaches that these compounds have analgesic and antipyretic properties and low toxicity. The compound of this patent of the formula



10

wherein R₃ is a hydrocarbon group may not have antioxidant activity since the effectiveness of p-aminophenols and other phenolics generally depends upon the presence of a free hydroxyl group, and the ethers and esters of these phenols generally have no significant effect.

15

U.S. Patent No. 4,038,434 to Young discloses that certain N-acyl-2,6-dialkyl-p-aminophenols are highly effective antioxidants for use with edible organic substances.

20

U.S. Patent No. 4,094,999 to Cohen and O'Connell discloses a food composition stabilized by the presence therein of a small proportion of a dialkyl pentaerythritol diphosphite.

U.S. Patent No. 4,363,910 to Ambrus, Szabolesi and Hutás disclose the use of 2,2-dimethyl-1,2-dihydroquinoline derivatives useful as antioxidants to stabilize animal feedstuffs.

25

U.S. Patent No. 5,084,289 to Shin, Han and Yi discloses a method for inhibiting the oxidation of edible oils and fats by forming a reverse miscelle by admixing a mixture of an aqueous solution containing tocopherol and ascorbic acid with a surfactant and said oils or fats.

- 3 -

U.S. Patent No. 3,778,464 to Klemchuk discloses substituted hydroxylamine antioxidants of the formula R_7R_8NOH wherein R_7 or R_8 is alkyl containing from 1 to 3 carbon atoms, benzyl, chlorobenzyl, nitrobenzyl, benzhydryl or triphenylmethyl with the proviso that only one of R_7 or R_8 is alkyl and that R_8 is hydrogen when R_7 is benzhydryl or triphenylmethyl, or R_7 and R_8 taken together with the nitrogen atom form a heterocyclic group such as morpholino, piperidino or piperazino. The compounds are stated to be useful for organic substances including fats and oils of animal fats and foods made therewith or therein.

Other antioxidants for food include those disclosed in U.S. Patent No. 5,527,552 to Todd, Jr. - green tea catechins; U.S. Patent No. 4,925,681 to Mai, Chambers and McDonald - extracts from black tea.

It is an object of the invention to provide food compositions having improved stability and containing antioxidant compositions which include one or more of the antioxidants disclosed herein.

It is a related object of this invention to provide a method of stabilizing food products through the addition thereto of antioxidant compositions which include one or more of the antioxidants of the present invention.

It is still another object of this invention to provide edible fat and oil compositions having improved stability and containing antioxidant compositions which include one or more of the antioxidants disclosed herein.

It is a still further object of this invention to provide a method of stabilizing edible fat and oil compositions through the addition thereto of antioxidant compositions which include one or more of the antioxidants of the present invention.

Summary of the Invention

It has now been found that a combination of one or more compounds selected from the group consisting of 3-arylbenzofuranones, long chain N,N-dialkylhydroxylamines, substituted hydroxylamines, nitrones, and amine oxides as defined hereinafter are highly effective antioxidants for use with edible organic substances subject to deterioration by oxidation.

- 4 -

Detailed Description

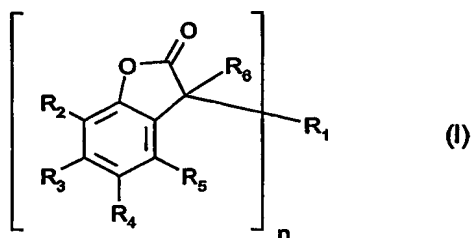
Edible organic substances that may be stabilized against oxidation include hydrocarbon-containing substances that are suitable for human or animal consumption, for example, frying
5 oils and fats, potato flakes, bakery products, meat emulsions, precooked cereals, instant noodles, soybean milk, chicken products, emulsion products such as sausage, mayonnaise and margarine, frozen fish, frozen pizza, cheese and animal foods.

The antioxidants of this invention are extremely useful in the stabilization of fats, fatty
10 alcohols, fatty acids, esters of fatty acids and fatty oils which may be essentially solid or liquid at room temperature, and may be hydrogenated or unhydrogenated as well as various foods containing or prepared in such products. The oils or fats may be naturally-occurring, such as animal or vegetable fats, or synthetic materials. Exemplary materials are tallow, lard, peanut oil, corn oil, cottonseed oil, olive oil, safflower oil, soybean oil, coconut oil,
15 shortening, cooking oils, salad oils and dressings, mayonaisse, margarine and the like. The fatty acid portion of such materials generally has at least about 12 carbon atoms, say up to about 24 or more carbon atoms per ester site, and the ester portions are frequently glycerides, although the materials may be other types of esters of various mono and polyhydroxy alkyl alcohols. Generally, the ester portions of the molecule have less than
20 about 12 carbon atoms, preferably less than about 6 carbon atoms, e.g. glycerides or other lower alkyl esters.

The 3-arylbenzofuranones antioxidants of the present invention are for example those disclosed in U.S. patent Nos. 4,325,863; U.S. 4,388,244; U.S. 5,175,312; U.S. 5,252,643;
25 U.S. 5,216,052; U.S. 5,369,159; U.S. 5,488,117; U.S. 5,356,966; U.S. 5,367,008; U.S. 5,428,162; U.S. 5,428,177; and U.S. 5,516,920; which are hereby incorporated by reference.

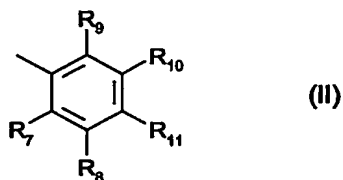
Particularly suitable 3-arylbenzofuranones in the present invention are compounds of the formula I

- 5 -



in which, if n is 1,

- R₁ is unsubstituted or C₁-C₄alkyl-, C₁-C₄alkoxy-, C₁-C₄alkylthio-, hydroxyl-, halo-, amino-, C₁-C₄alkylamino-, phenylamino- or di(C₁-C₄alkyl)amino-substituted naphthyl, phenanthryl, anthryl, 5,6,7,8-tetrahydro-2-naphthyl, 5,6,7,8-tetrahydro-1-naphthyl, thienyl, benzo[b]thienyl, naphtho[2,3-b]thienyl, thianthrenyl, dibenzofuryl, chromenyl, xanthenyl, phenoxathinyl, pyrrolyl, imidazolyl, pyrazolyl, pyrazinyl, pyrimidinyl, pyridazinyl, indolizynyl, isoindolyl, indolyl, indazolyl, purinyl, quinolizynyl, isoquinolyl, quinolyl, phthalazinyl, naphthyridinyl, quinoxalynyl, quinazolinyl, cinnolinyl, pteridinyl, carbazolyl, β-carbolinyl, phenanthridinyl, acridinyl, perimidinyl, phenanthrolinyl, phenazinyl, isothiazolyl, phenothiazinyl, isoxazolyl, furazanyl, biphenyl, terphenyl, fluorenyl or phenoxazinyl, or R₁ is a radical of the formula II



and

if n is 2,

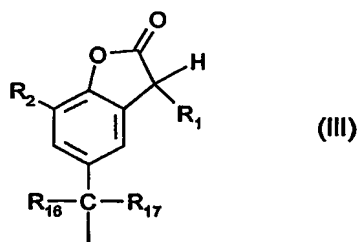
- R₁ is unsubstituted or C₁-C₄alkyl- or hydroxy-substituted phenylene or naphthylene; or is -R₁₂-X-R₁₃-,
 R₂, R₃, R₄ and R₅ independently of one another are hydrogen, chlorine, hydroxyl, C₁-C₂₅alkyl, C₇-C₉phenylalkyl, unsubstituted or C₁-C₄alkyl-substituted phenyl; unsubstituted or C₁-C₄alkyl-substituted C₅-C₈cycloalkyl; C₁-C₁₈alkoxy, C₁-C₁₈alkylthio, C₁-C₄alkylamino, di(C₁-C₄alkyl)amino, C₁-C₂₅alkanoyloxy, C₁-C₂₅alkanoylamino, C₃-C₂₅alkenoyloxy,

C₃-C₂₅alkanoyloxy which is interrupted by oxygen, sulfur or >N-R_{14} ; C₆-C₉cycloalkyl-

carbonyloxy, benzoyloxy or C₁-C₁₂alkyl-substituted benzoyloxy; or else the radicals R₂ and R₃ or the radicals R₃ and R₄ or the radicals R₄ and R₅, together with the carbon atoms to which

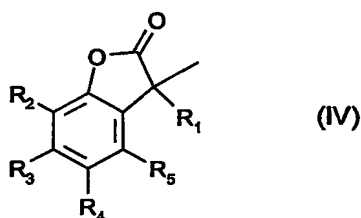
- 6 -

they are attached, form a benzo ring, R_4 is additionally $-(CH_2)_p-COR_{15}$ or $-(CH_2)_qOH$ or, if R_3 , R_5 and R_6 are hydrogen, R_4 is additionally a radical of the formula III



in which R_1 is defined as indicated above for $n = 1$,

5 R_6 is hydrogen or a radical of the formula IV



where R_4 is not a radical of the formula III and R_1 is defined as indicated above for $n = 1$, R_7 , R_8 , R_9 , R_{10} and R_{11} independently of one another are hydrogen, halogen, hydroxyl,

C_1 - C_{25} alkyl, C_2 - C_{25} alkyl interrupted by oxygen, sulfur or $\text{>N}-R_{14}$; C_1 - C_{25} alkoxy,

10 C_2 - C_{25} alkoxy interrupted by oxygen, sulfur or $\text{>N}-R_{14}$; C_1 - C_{25} alkylthio, C_3 - C_{25} alkenyl, C_3 -

C_{25} alkenyloxy, C_3 - C_{25} alkynyl, C_3 - C_{25} alkynyloxy, C_7 - C_9 phenylalkyl, C_7 - C_9 phenylalkoxy, unsubstituted or C_1 - C_4 alkyl-substituted phenyl; unsubstituted or C_1 - C_4 alkyl-substituted phenoxy; unsubstituted or C_1 - C_4 alkyl-substituted C_5 - C_8 cycloalkyl; unsubstituted or C_1 - C_4 alkyl-substituted C_5 - C_8 cycloalkoxy; C_1 - C_4 alkylamino, di(C_1 - C_4 alkyl)amino, C_1 - C_{25} alkanoyl, C_3 -

15 C_{25} alkanoyl interrupted by oxygen, sulfur or $\text{>N}-R_{14}$; C_1 - C_{25} alkanoyloxy, C_3 -

C_{25} alkanoyloxy interrupted by oxygen, sulfur or $\text{>N}-R_{14}$; C_1 - C_{25} alkanoylamino, C_3 -

- 7 -

C₂₅alkenoyl, C₃-C₂₅alkenoyl interrupted by oxygen, sulfur or >N-R_{14} ; C₃-C₂₅alkenoyloxy,

C₃-C₂₅alkenoyloxy interrupted by oxygen, sulfur or >N-R_{14} ; C₆-C₉cycloalkylcarbonyl, C₆-

C₉cycloalkylcarbonyloxy, benzoyl or C₁-C₁₂alkyl-substituted benzoyl; benzoyloxy or C₁-

C₁₂alkyl-substituted benzoyloxy; $\text{—O—}\overset{\overset{\text{R}_{18}}{|}}{\underset{\underset{\text{R}_{19}}{|}}{\text{C}}}\text{—}\overset{\overset{\text{O}}{||}}{\text{C}}\text{—R}_{15}$ or $\text{—O—}\overset{\overset{\text{R}_{20}}{|}}{\underset{\underset{\text{H}}{|}}{\text{C}}}\text{—}\overset{\overset{\text{R}_{21}}{|}}{\underset{\underset{\text{R}_{22}}{|}}{\text{C}}}\text{—O—R}_{23}$, or

- 5 else, in formula II, the radicals R₇ and R₈ or the radicals R₈ and R₁₁, together with the carbon atoms to which they are attached, form a benzo ring,

R₁₂ and R₁₃ independently of one another are unsubstituted or C₁-C₄alkyl-substituted phenylene or naphthylene,

R₁₄ is hydrogen or C₁-C₈alkyl,

- 10 R₁₅ is hydroxyl, $\left[\text{—O}^- \frac{1}{r} \text{M}^{r+} \right]$, C₁-C₁₈alkoxy or $\text{—N}\begin{matrix} \text{R}_{24} \\ \text{R}_{25} \end{matrix}$,

R₁₆ and R₁₇ independently of one another are hydrogen, CF₃, C₁-C₁₂alkyl or phenyl, or R₁₆ and R₁₇, together with the C atom to which they are attached, form a C₅-C₈cycloalkylidene ring which is unsubstituted or substituted from 1 to 3 times by C₁-C₄alkyl;

R₁₈ and R₁₉ independently of one another are hydrogen, C₁-C₄alkyl or phenyl,

- 15 R₂₀ is hydrogen or C₁-C₄alkyl,

R₂₁ is hydrogen, unsubstituted or C₁-C₄alkyl-substituted phenyl; C₁-C₂₅alkyl, C₂-C₂₅alkyl

interrupted by oxygen, sulfur or >N-R_{14} ; C₇-C₉phenylalkyl which is unsubstituted or

substituted on the phenyl radical from 1 to 3 times by C₁-C₄alkyl; C₇-C₂₅phenylalkyl which is unsubstituted or substituted on the phenyl radical from 1 to 3 times by C₁-C₄alkyl and

- 20 interrupted by oxygen, sulfur or >N-R_{14} , or else the radicals R₂₀ and R₂₁, together with

the carbon atoms to which they are attached, form a C₅-C₁₂cycloalkylene ring which is unsubstituted or substituted from 1 to 3 times by C₁-C₄alkyl;

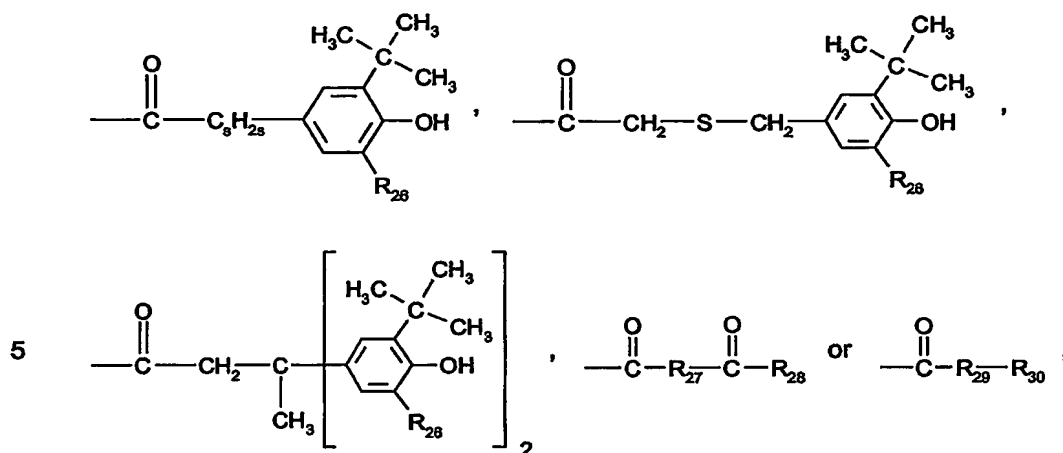
R₂₂ is hydrogen or C₁-C₄alkyl,

- 8 -

R_{23} is hydrogen, C_1 - C_{25} alkanoyl, C_3 - C_{25} alkenoyl, C_3 - C_{25} alkanoyl interrupted by oxygen, sulfur

or $\text{N}-R_{14}$; C_2 - C_{25} alkanoyl substituted by a di(C_1 - C_6 alkyl)phosphonate group;

C_6 - C_8 cycloalkylcarbonyl, thenoyl, furoyl, benzoyl or C_1 - C_{12} alkyl-substituted benzoyl;



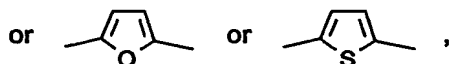
R_{24} and R_{25} independently of one another are hydrogen or C_1 - C_{18} alkyl,

R_{26} is hydrogen or C_1 - C_8 alkyl,

R_{27} is a direct bond, C_1 - C_{18} alkylene, C_2 - C_{18} alkylene interrupted by oxygen, sulfur or

$\text{N}-R_{14}$; C_2 - C_{18} alkenylene, C_2 - C_{20} alkylidene, C_7 - C_{20} phenylalkylidene,

10 C_5 - C_8 cycloalkylene, C_7 - C_8 bicycloalkylene, unsubstituted or C_1 - C_4 alkyl-substituted phenylene,



R_{28} is hydroxyl, $\left[-O^- \frac{1}{r} M^{r+} \right]$, C_1 - C_{18} alkoxy or $\text{N}-R_{24}$,

R_{29} is oxygen, -NH- or $\text{N}-\text{C}(=\text{O})-\text{NH}-R_{30}$,

R_{30} is C_1 - C_{18} alkyl or phenyl,

15 R_{31} is hydrogen or C_1 - C_{18} alkyl,

- 9 -

M is an r-valent metal cation,

X is a direct bond, oxygen, sulfur or -NR₃₁-,

n is 1 or 2,

p is 0, 1 or 2,

5 q is 1, 2, 3, 4, 5 or 6,

r is 1, 2 or 3, and

s is 0, 1 or 2.

Unsubstituted or C₁-C₄alkyl-, C₁-C₄alkoxy-, C₁-C₄alkylthio-, hydroxyl-, halo-, amino-,
 10 C₁-C₄alkylamino-, phenylamino- or di(C₁-C₄alkyl)amino-substituted naphthyl, phenanthryl,
 anthryl, 5,6,7,8-tetrahydro-2-naphthyl, 5,6,7,8-tetrahydro-1-naphthyl, thienyl, benzo[b]thienyl,
 naphtho[2,3-b]thienyl, thianthrenyl, dibenzofuryl, chromenyl, xanthenyl, phenoxathiinyl,
 pyrrolyl, imidazolyl, pyrazolyl, pyrazinyl, pyrimidinyl, pyridazinyl, indolizynyl, isoindolyl, indolyl,
 indazolyl, purinyl, quinolizynyl, isoquinolyl, quinolyl, phthalazinyl, naphthyridinyl, quinoxalynyl,
 15 quinazolinyl, cinnolinyl, pteridinyl, carbazolyl, β-carbolinyl, phenanthridinyl, acridinyl,
 perimidinyl, phenanthrolinyl, phenazinyl, isothiazolyl, phenothiazinyl, isoxazolyl, furazanyl,
 biphenyl, terphenyl, fluorenyl or phenoxazinyl is, for example, 1-naphthyl, 2-naphthyl,
 1-phenylamino-4-naphthyl, 1-methylnaphthyl, 2-methylnaphthyl, 1-methoxy-2-naphthyl,
 2-methoxy-1-naphthyl, 1-dimethylamino-2-naphthyl, 1,2-dimethyl-4-naphthyl, 1,2-dimethyl-6-
 20 naphthyl, 1,2-dimethyl-7-naphthyl, 1,3-dimethyl-6-naphthyl, 1,4-dimethyl-6-naphthyl,
 1,5-dimethyl-2-naphthyl, 1,6-dimethyl-2-naphthyl, 1-hydroxy-2-naphthyl, 2-hydroxy-1-
 naphthyl, 1,4-dihydroxy-2-naphthyl, 7-phenanthryl, 1-anthryl, 2-anthryl, 9-anthryl,
 3-benzo[b]thienyl, 5-benzo[b]thienyl, 2-benzo[b]thienyl, 4-dibenzofuryl, 4,7-dibenzofuryl,
 4-methyl-7-dibenzofuryl, 2-xanthenyl, 8-methyl-2-xanthenyl, 3-xanthenyl, 2-phenoxathiinyl,
 25 2,7-phenoxathiinyl, 2-pyrrolyl, 3-pyrrolyl, 5-methyl-3-pyrrolyl, 2-imidazolyl, 4-imidazolyl,
 5-imidazolyl, 2-methyl-4-imidazolyl, 2-ethyl-4-imidazolyl, 2-ethyl-5-imidazolyl, 3-pyrazolyl,
 1-methyl-3-pyrazolyl, 1-propyl-4-pyrazolyl, 2-pyrazinyl, 5,6-dimethyl-2-pyrazinyl, 2-indolizynyl,
 2-methyl-3-isoindolyl, 2-methyl-1-isoindolyl, 1-methyl-2-indolyl, 1-methyl-3-indolyl,
 1,5-dimethyl-2-indolyl, 1-methyl-3-indazolyl, 2,7-dimethyl-8-purinyl, 2-methoxy-7-methyl-8-
 30 purinyl, 2-quinolizynyl, 3-isoquinolyl, 6-isoquinolyl, 7-isoquinolyl, isoquinolyl, 3-methoxy-6-
 isoquinolyl, 2-quinolyl, 6-quinolyl, 7-quinolyl, 2-methoxy-3-quinolyl, 2-methoxy-6-quinolyl,
 6-phthalazinyl, 7-phthalazinyl, 1-methoxy-6-phthalazinyl, 1,4-dimethoxy-6-phthalazinyl,
 1,8-naphthyridin-2-yl, 2-quinoxalynyl, 6-quinoxalynyl, 2,3-dimethyl-6-quinoxalynyl, 2,3-di-
 methoxy-6-quinoxalynyl, 2-quinazolinyl, 7-quinazolinyl, 2-dimethylamino-6-quinazolinyl,

- 10 -

- 3-cinnolinyl, 6-cinnolinyl, 7-cinnolinyl, 3-methoxy-7-cinnolinyl, 2-pteridinyl, 6-pteridinyl, 7-pteridinyl, 6,7-dimethoxy-2-pteridinyl, 2-carbazolyl, 3-carbazolyl, 9-methyl-2-carbazolyl, 9-methyl-3-carbazolyl, β -carbolin-3-yl, 1-methyl- β -carbolin-3-yl, 1-methyl- β -carbolin-6-yl, 3-phenanthridinyl, 2-acridinyl, 3-acridinyl, 2-perimidinyl, 1-methyl-5-perimidinyl,
- 5 5-phenanthrolinyl, 6-phenanthrolinyl, 1-phenazinyl, 2-phenazinyl, 3-isothiazolyl, 4-isothiazolyl, 5-isothiazolyl, 2-phenothiazinyl, 3-phenothiazinyl, 10-methyl-3-phenothiazinyl, 3-isoxazolyl, 4-isoxazolyl, 5-isoxazolyl, 4-methyl-3-furazanyl, 2-phenoxazinyl or 10-methyl-2-phenoxazinyl.
- 10 Particular preference is given to unsubstituted or C₁-C₄alkyl-, C₁-C₄alkoxy-, C₁-C₄alkylthio-, hydroxyl-, phenylamino- or di(C₁-C₄alkyl)amino-substituted naphthyl, phenanthryl, anthryl, 5,6,7,8-tetrahydro-2-naphthyl, 5,6,7,8-tetrahydro-1-naphthyl, thienyl, benzo[b]thienyl, naphtho[2,3-b]thienyl, thianthrenyl, dibenzofuryl, chromenyl, xanthenyl, phenoxathiinyl, pyrrolyl, isoindolyl, indolyl, phenothiazinyl, biphenyl, terphenyl, fluorenyl or phenoxazinyl such as, for
- 15 example, 1-naphthyl, 2-naphthyl, 1-phenylamino-4-naphthyl, 1-methylnaphthyl, 2-methylnaphthyl, 1-methoxy-2-naphthyl, 2-methoxy-1-naphthyl, 1-dimethylamino-2-naphthyl, 1,2-dimethyl-4-naphthyl, 1,2-dimethyl-6-naphthyl, 1,2-dimethyl-7-naphthyl, 1,3-dimethyl-6-naphthyl, 1,4-dimethyl-6-naphthyl, 1,5-dimethyl-2-naphthyl, 1,6-dimethyl-2-naphthyl, 1-hydroxy-2-naphthyl, 2-hydroxy-1-naphthyl, 1,4-dihydroxy-2-naphthyl, 7-phenanthryl, 1-anthryl, 2-anthryl,
- 20 9-anthryl, 3-benzo[b]thienyl, 5-benzo[b]thienyl, 2-benzo[b]thienyl, 4-dibenzofuryl, 4,7-dibenzofuryl, 4-methyl-7-dibenzofuryl, 2-xanthenyl, 8-methyl-2-xanthenyl, 3-xanthenyl, 2-pyrrolyl, 3-pyrrolyl, 2-phenothiazinyl, 3-phenothiazinyl, 10-methyl-3-phenothiazinyl.

Halogen (halo) is, for example, chlorine, bromine or iodine. Preference is given to chlorine.

25

Alkanoyl having up to 25 carbon atoms is a branched or unbranched radical such as, for example, formyl, acetyl, propionyl, butanoyl, pentanoyl, hexanoyl, heptanoyl, octanoyl, nonanoyl, decanoyl, undecanoyl, dodecanoyl, tridecanoyl, tetradecanoyl, pentadecanoyl, hexadecanoyl, heptadecanoyl, octadecanoyl, eicosanoyl or docosanoyl. Preference is given to al-

30 kanoyl having 2 to 18, especially 2 to 12, for example 2 to 6 carbon atoms. Particular preference is given to acetyl.

C₂-C₂₅alkanoyl substituted by a di(C₁-C₈alkyl)phosphonate group is, for example, (CH₃CH₂O)₂POCH₂CO-, (CH₃O)₂POCH₂CO-, (CH₃CH₂CH₂CH₂O)₂POCH₂CO-,

- 11 -

$(\text{CH}_3\text{CH}_2\text{O})_2\text{POCH}_2\text{CH}_2\text{CO}-$, $(\text{CH}_3\text{O})_2\text{POCH}_2\text{CH}_2\text{CO}-$, $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_2\text{POCH}_2\text{CH}_2\text{CO}-$,
 $(\text{CH}_3\text{CH}_2\text{O})_2\text{PO}(\text{CH}_2)_4\text{CO}-$, $(\text{CH}_3\text{CH}_2\text{O})_2\text{PO}(\text{CH}_2)_8\text{CO}-$ or $(\text{CH}_3\text{CH}_2\text{O})_2\text{PO}(\text{CH}_2)_{17}\text{CO}-$.

Alkanoyloxy having up to 25 carbon atoms is a branched or unbranched radical such as, for
 5 example, formyloxy, acetoxy, propionyloxy, butanoyloxy, pentanoyloxy, hexanoyloxy, hepta-
 noyloxy, octanoyloxy, nonanoyloxy, decanoyloxy, undecanoyloxy, dodecanoyloxy, trideca-
 noyloxy, tetradecanoyloxy, pentadecanoyloxy, hexadecanoyloxy, heptadecanoyloxy, octa-
 decanoyloxy, eicosanoyloxy or docosanoyloxy. Preference is given to alkanoyloxy having 2
 to 18, especially 2 to 12, for example 2 to 6 carbon atoms. Particular preference is given to
 10 acetoxy.

Alkenoyl having 3 to 25 carbon atoms is a branched or unbranched radical such as, for
 example, propenoyl, 2-butenoyl, 3-butenoyl, isobutenoyl, n-2,4-pentadienoyl, 3-methyl-2-bu-
 tenoyl, n-2-octenoyl, n-2-dodecenoyl, iso-dodecenoyl, oleoyl, n-2-octadecenoyl or n-4-octa-
 15 decenoyl. Preference is given to alkenoyl having 3 to 18, especially 3 to 12, for example 3 to
 6, in particular 3 to 4 carbon atoms.

$\text{C}_3\text{-C}_{25}$ alkenoyl interrupted by oxygen, sulfur or $\text{N}-\text{R}_{14}$ is, for example,

$\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}=\text{CHCO}-$ or $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}=\text{CHCO}-$.

20

Alkenoyloxy having 3 to 25 carbon atoms is a branched or unbranched radical such as, for
 example, propenoyloxy, 2-butenoyloxy, 3-butenoyloxy, isobutenoyloxy, n-2,4-pentadienoyl-
 oxy, 3-methyl-2-butenoyloxy, n-2-octenoyloxy, n-2-dodecenoyloxy, iso-dodecenoyloxy,
 oleoyloxy, n-2-octadecenoyloxy or n-4-octadecenoyloxy. Preference is given to alkenoyloxy
 25 having 3 to 18, especially 3 to 12, for example 3 to 6, in particular 3 to 4 carbon atoms.

$\text{C}_3\text{-C}_{25}$ alkenoyloxy interrupted by oxygen, sulfur or $\text{N}-\text{R}_{14}$ is, for example,

$\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}=\text{CHCOO}-$ or $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}=\text{CHCOO}-$.

- 12 -

C₃-C₂₅alkanoyl interrupted by oxygen, sulfur or $\text{N}-\text{R}_{14}$ is, for example, CH₃-O-CH₂CO-,
 , CH₃-S-CH₂CO-, CH₃-NH-CH₂CO-, CH₃-N(CH₃)-CH₂CO-, CH₃-O-CH₂CH₂-O-CH₂CO-,
 CH₃-(O-CH₂CH₂)₂O-CH₂CO-, CH₃-(O-CH₂CH₂)₃O-CH₂CO- or CH₃-(O-CH₂CH₂)₄O-CH₂CO-.

5 C₃-C₂₅alkanoyloxy interrupted by oxygen, sulfur or $\text{N}-\text{R}_{14}$ is, for example,

CH₃-O-CH₂COO-, CH₃-S-CH₂COO-, CH₃-NH-CH₂COO-, CH₃-N(CH₃)-CH₂COO-,
 CH₃-O-CH₂CH₂-O-CH₂COO-, CH₃-(O-CH₂CH₂)₂O-CH₂COO-, CH₃-(O-CH₂CH₂)₃O-CH₂COO-
 or CH₃-(O-CH₂CH₂)₄O-CH₂COO-.

10 C₆-C₉cycloalkylcarbonyl is, for example, cyclopentylcarbonyl, cyclohexylcarbonyl, cycloheptylcarbonyl or cyclooctylcarbonyl. Cyclohexylcarbonyl is preferred.

C₆-C₉cycloalkylcarbonyloxy is, for example, cyclopentylcarbonyloxy, cyclohexylcarbonyloxy, cycloheptylcarbonyloxy or cyclooctylcarbonyloxy. Cyclohexylcarbonyloxy is preferred.

15

C₁-C₁₂alkyl-substituted benzoyl, which preferably carries 1 to 3, especially 1 or 2 alkyl groups, is, for example, o-, m- or p-methylbenzoyl, 2,3-dimethylbenzoyl, 2,4-dimethylbenzoyl, 2,5-dimethylbenzoyl, 2,6-dimethylbenzoyl, 3,4-dimethylbenzoyl, 3,5-dimethylbenzoyl, 2-methyl-6-ethylbenzoyl, 4-tert-butylbenzoyl, 2-ethylbenzoyl, 2,4,6-trimethylbenzoyl, 2,6-dimethyl-4-tert-butylbenzoyl or 3,5-di-tert-butylbenzoyl. Preferred substituents are C₁-C₈alkyl, especially C₁-C₄alkyl.

20

C₁-C₁₂alkyl-substituted benzoyloxy, which preferably carries 1 to 3, especially 1 or 2 alkyl groups, is, for example, o-, m- or p-methylbenzoyloxy, 2,3-dimethylbenzoyloxy, 2,4-dimethylbenzoyloxy, 2,5-dimethylbenzoyloxy, 2,6-dimethylbenzoyloxy, 3,4-dimethylbenzoyloxy, 3,5-dimethylbenzoyloxy, 2-methyl-6-ethylbenzoyloxy, 4-tert-butylbenzoyloxy, 2-ethylbenzoyloxy, 2,4,6-trimethylbenzoyloxy, 2,6-dimethyl-4-tert-butylbenzoyloxy or 3,5-di-tert-butylbenzoyloxy. Preferred substituents are C₁-C₈alkyl, especially C₁-C₄alkyl.

25

30 Alkyl having up to 25 carbon atoms is a branched or unbranched radical such as, for example, methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, 2-ethylbutyl,

- 13 -

n-pentyl, isopentyl, 1-methylpentyl, 1,3-dimethylbutyl, n-hexyl, 1-methylhexyl, n-heptyl, isoheptyl, 1,1,3,3-tetramethylbutyl, 1-methylheptyl, 3-methylheptyl, n-octyl, 2-ethylhexyl, 1,1,3-trimethylhexyl, 1,1,3,3-tetramethylpentyl, nonyl, decyl, undecyl, 1-methylundecyl, dodecyl, 1,1,3,3,5,5-hexamethylhexyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, eicosyl or docosyl. One of the preferred meanings of R_2 and R_4 is, for example, C_1 - C_{18} alkyl. A particularly preferred meaning of R_4 is C_1 - C_4 alkyl.

Alkenyl having 3 to 25 carbon atoms is a branched or unbranched radical such as, for example, propenyl, 2-butenyl, 3-butenyl, isobutenyl, n-2,4-pentadienyl, 3-methyl-2-butenyl, n-2-octenyl, n-2-dodecenyl, iso-dodecenyl, oleyl, n-2-octadecenyl or n-4-octadecenyl. Preference is given to alkenyl having 3 to 18, especially 3 to 12, for example 3 to 6, in particular 3 to 4 carbon atoms.

Alkenyloxy having 3 to 25 carbon atoms is a branched or unbranched radical such as, for example, propenyloxy, 2-butenyloxy, 3-butenyloxy, isobutenyloxy, n-2,4-pentadienyloxy, 3-methyl-2-butenyloxy, n-2-octenyloxy, n-2-dodecenyloxy, iso-dodecenyloxy, oleyloxy, n-2-octadecenyloxy or n-4-octadecenyloxy. Preference is given to alkenyloxy having 3 to 18, especially 3 to 12, for example 3 to 6, in particular 3 to 4 carbon atoms.

Alkynyl having 3 to 25 carbon atoms is a branched or unbranched radical such as, for example, propynyl ($-\text{CH}_2-\text{C}\equiv\text{CH}$), 2-butylnyl, 3-butylnyl, n-2-octynyl, or n-2-dodecynyl. Preference is given to alkynyl having 3 to 18, especially 3 to 12, for example 3 to 6, in particular 3 to 4 carbon atoms.

Alkynyloxy having 3 to 25 carbon atoms is a branched or unbranched radical such as, for example, propynyloxy ($-\text{OCH}_2-\text{C}\equiv\text{CH}$), 2-butyynyloxy, 3-butyynyloxy, n-2-octynyloxy, or n-2-dodecynyloxy. Preference is given to alkynyloxy having 3 to 18, especially 3 to 12, for example 3 to 6, in particular 3 to 4 carbon atoms.

- 14 -

C₂-C₂₅alkyl interrupted by oxygen, sulfur or $\begin{array}{c} \diagup \\ \text{N}-\text{R}_{14} \\ \diagdown \end{array}$ is, for example, CH₃-O-CH₂-

CH₃-S-CH₂-, CH₃-NH-CH₂-, CH₃-N(CH₃)-CH₂-, CH₃-O-CH₂CH₂-O-CH₂-,
CH₃-(O-CH₂CH₂)₂-O-CH₂-, CH₃-(O-CH₂CH₂)₃-O-CH₂- or CH₃-(O-CH₂CH₂)₄-O-CH₂-.

- 5 C₇-C₉phenylalkyl is, for example, benzyl, α-methylbenzyl, α,α-dimethylbenzyl or 2-phenyl-ethyl. Benzyl and α,α-dimethylbenzyl are preferred.

- C₇-C₉phenylalkyl which is unsubstituted or substituted on the phenyl radical from 1 to 3 times
by C₁-C₄alkyl is, for example, benzyl, α-methylbenzyl, α,α-dimethylbenzyl, 2-phenylethyl,
10 2-methylbenzyl, 3-methylbenzyl, 4-methylbenzyl, 2,4-dimethylbenzyl, 2,6-dimethylbenzyl or
4-tert-butylbenzyl. Benzyl is preferred.

C₇-C₂₅phenylalkyl which is unsubstituted or substituted on the phenyl radical from 1 to 3

times by C₁-C₄alkyl and is interrupted by oxygen, sulfur or $\begin{array}{c} \diagup \\ \text{N}-\text{R}_{14} \\ \diagdown \end{array}$ is a branched or un-

- 15 branched radical such as, for example, phenoxymethyl, 2-methylphenoxymethyl, 3-methyl-
phenoxymethyl, 4-methylphenoxymethyl, 2,4-dimethylphenoxymethyl, 2,3-dimethylphenoxy-
methyl, phenylthiomethyl, N-methyl-N-phenylmethyl, N-ethyl-N-phenylmethyl, 4-tert-butyl-
phenoxymethyl, 4-tert-butylphenoxyethoxymethyl, 2,4-di-tert-butylphenoxymethyl, 2,4-di-tert-
butylphenoxyethoxymethyl, phenoxyethoxyethoxyethoxymethyl, benzyloxymethyl, benzyloxy-
20 ethoxymethyl, N-benzyl-N-ethylmethyl or N-benzyl-N-isopropylmethyl.

C₇-C₉phenylalkoxy is, for example, benzyloxy, α-methylbenzyloxy, α,α-dimethylbenzyloxy or
2-phenylethoxy. Benzyloxy is preferred.

- 25 C₁-C₄alkyl-substituted phenyl, which preferably contains 1 to 3, especially 1 or 2 alkyl groups,
is, for example, o-, m- or p-methylphenyl, 2,3-dimethylphenyl, 2,4-dimethylphenyl, 2,5-
dimethylphenyl, 2,6-dimethylphenyl, 3,4-dimethylphenyl, 3,5-dimethylphenyl, 2-methyl-6-
ethylphenyl, 4-tert-butylphenyl, 2-ethylphenyl or 2,6-diethylphenyl.

- 15 -

C₁-C₄alkyl-substituted phenoxy, which preferably contains 1 to 3, especially 1 or 2 alkyl groups, is, for example, o-, m- or p-methylphenoxy, 2,3-dimethylphenoxy, 2,4-dimethylphenoxy, 2,5-dimethylphenoxy, 2,6-dimethylphenoxy, 3,4-dimethylphenoxy, 3,5-dimethylphenoxy, 2-methyl-6-ethylphenoxy, 4-tert-butylphenoxy, 2-ethylphenoxy or 2,6-diethylphenoxy.

5

Unsubstituted or C₁-C₄alkyl-substituted C₅-C₈cycloalkyl is, for example, cyclopentyl, methylcyclopentyl, dimethylcyclopentyl, cyclohexyl, methylcyclohexyl, dimethylcyclohexyl, trimethylcyclohexyl, tert-butylcyclohexyl, cycloheptyl or cyclooctyl. Preference is given to cyclohexyl and tert-butylcyclohexyl.

10

Unsubstituted or C₁-C₄alkyl-substituted C₅-C₈cycloalkoxy is, for example, cyclopentoxo, methylcyclopentoxo, dimethylcyclopentoxo, cyclohexoxo, methylcyclohexoxo, dimethylcyclohexoxo, trimethylcyclohexoxo, tert-butylcyclohexoxo, cycloheptoxo or cyclooctoxo. Preference is given to cyclohexoxo and tert-butylcyclohexoxo.

15

Alkoxy having up to 25 carbon atoms is a branched or unbranched radical such as, for example, methoxy, ethoxy, propoxy, isopropoxy, n-butoxy, isobutoxy, pentoxy, isopentoxy, hexoxy, heptoxy, octoxy, decyloxy, tetradecyloxy, hexadecyloxy or octadecyloxy. Preference is given to alkoxy having 1 to 12, especially 1 to 8, for example 1 to 6 carbon atoms.

20

C₂-C₂₅alkoxy interrupted by oxygen, sulfur or >N-R_{14} is, for example,

CH₃-O-CH₂CH₂O-, CH₃-S-CH₂CH₂O-, CH₃-NH-CH₂CH₂O-, CH₃-N(CH₃)-CH₂CH₂O-,
CH₃-O-CH₂CH₂-O-CH₂CH₂O-, CH₃-(O-CH₂CH₂)₂O-CH₂CH₂O-,
CH₃-(O-CH₂CH₂)₃O-CH₂CH₂O- or CH₃-(O-CH₂CH₂)₄O-CH₂CH₂O-.

25

Alkylthio having up to 25 carbon atoms is a branched or unbranched radical such as, for example, methylthio, ethylthio, propylthio, isopropylthio, n-butylthio, isobutylthio, pentylthio, isopentylthio, hexylthio, heptylthio, octylthio, decylthio, tetradecylthio, hexadecylthio or octadecylthio. Preference is given to alkylthio having 1 to 12, especially 1 to 8, for example 1 to 6 carbon atoms.

30

- 16 -

Alkylamino having up to 4 carbon atoms is a branched or unbranched radical such as, for example, methylamino, ethylamino, propylamino, isopropylamino, n-butylamino, isobutylamino or tert-butylamino.

- 5 Di(C₁-C₄alkyl)amino also means that the two radicals independently of one another are branched or unbranched, such as, for example, dimethylamino, methylethylamino, diethylamino, methyl-n-propylamino, methylisopropylamino, methyl-n-butylamino, methylisobutylamino, ethylisopropylamino, ethyl-n-butylamino, ethylisobutylamino, ethyl-tert-butylamino, diethylamino, diisopropylamino, isopropyl-n-butylamino, isopropylisobutylamino, di-n-butylamino or diisobutylamino.
- 10

- Alkanoylamino having up to 25 carbon atoms is a branched or unbranched radical such as, for example, formylamino, acetylamino, propionylamino, butanoylamino, pentanoylamino, hexanoylamino, heptanoylamino, octanoylamino, nonanoylamino, decanoylamino, undecanoylamino, dodecanoylamino, tridecanoylamino, tetradecanoylamino, pentadecanoylamino, hexadecanoylamino, heptadecanoylamino, octadecanoylamino, eicosanoylamino or docosanoylamino. Preference is given to alkanoylamino having 2 to 18, especially 2 to 12, for example 2 to 6 carbon atoms.
- 15

- 20 C₁-C₁₈alkylene is a branched or unbranched radical such as, for example, methylene, ethylene, propylene, trimethylene, tetramethylene, pentamethylene, hexamethylene, heptamethylene, octamethylene, decamethylene, dodecamethylene or octadecamethylene. Preference is given to C₁-C₁₂alkylene, especially C₁-C₈alkylene.

- 25 A C₁-C₄alkyl-substituted C₅-C₁₂cycloalkylene ring, which preferably contains 1 to 3, especially 1 or 2 branched or unbranched alkyl group radicals is, for example, cyclopentylene, methylcyclopentylene, dimethylcyclopentylene, cyclohexylene, methylcyclohexylene, dimethylcyclohexylene, trimethylcyclohexylene, tert-butylcyclohexylene, cycloheptylene, cyclooctylene or cyclodecylene. Preference is given to cyclohexylene and tert-butylcyclohexylene.
- 30

C₂-C₁₈alkylene interrupted by oxygen, sulfur or $\begin{array}{c} \diagup \\ \text{N} \\ \diagdown \end{array} \text{---R}_{14}$ is, for example, -CH₂-O-CH₂-, -CH₂-S-CH₂-, -CH₂-NH-CH₂-, -CH₂-N(CH₃)-CH₂-, -CH₂-O-CH₂CH₂-O-CH₂-,

- 17 -

$-\text{CH}_2-(\text{O}-\text{CH}_2\text{CH}_2)_2\text{O}-\text{CH}_2-$, $-\text{CH}_2-(\text{O}-\text{CH}_2\text{CH}_2)_3\text{O}-\text{CH}_2-$, $-\text{CH}_2-(\text{O}-\text{CH}_2\text{CH}_2)_4\text{O}-\text{CH}_2-$ or $-\text{CH}_2\text{CH}_2-\text{S}-\text{CH}_2\text{CH}_2-$.

5 C_2-C_{18} alkenylene is, for example, vinylene, methylvinylene, octenylethylene or dodecenylethylene. Preference is given to C_2-C_8 alkenylene.

10 Alkylidene having 2 to 20 carbon atoms is, for example, ethylidene, propylidene, butylidene, pentylidene, 4-methylpentylidene, heptylidene, nonylidene, tridecylidene, nonadecylidene, 1-methylethylidene, 1-ethylpropylidene or 1-ethylpentylidene. Preference is given to C_2-C_8 alkylidene.

Phenylalkylidene having 7 to 20 carbon atoms is, for example, benzylidene, 2-phenylethylidene or 1-phenyl-2-hexylidene. Preference is given to C_7-C_9 -phenylalkylidene.

15 C_5-C_8 cycloalkylene is a saturated hydrocarbon group having two free valencies and at least one ring unit and is, for example, cyclopentylene, cyclohexylene, cycloheptylene or cyclooctylene. Preference is given to cyclohexylene.

C_7-C_8 bicycloalkylene is, for example, bicycloheptylene or bicyclooctylene.

20 Unsubstituted or C_1-C_4 alkyl-substituted phenylene or naphthylene is, for example, 1,2-, 1,3-, 1,4-phenylene, 1,2-, 1,3-, 1,4-, 1,6-, 1,7-, 2,6- or 2,7-naphthylene. 1,4-Phenylene is preferred.

25 A C_1-C_4 alkyl-substituted C_5-C_8 cycloalkylidene ring, which preferably contains 1 to 3, especially 1 or 2 branched or unbranched alkyl group radicals is, for example, cyclopentylidene, methylcyclopentylidene, dimethylcyclopentylidene, cyclohexylidene, methylcyclohexylidene, dimethylcyclohexylidene, trimethylcyclohexylidene, tert-butylcyclohexylidene, cycloheptylidene or cyclooctylidene. Preference is given to cyclohexylidene and tert-butylcyclohexylidene.
30

A mono-, di- or trivalent metal cation is preferably an alkali metal, alkaline earth metal or aluminium cation, for example, Na^+ , K^+ , Mg^{++} , Ca^{++} or Al^{+++} .

- 18 -

A particularly preferred composition of present invention contains at least one compound of formula I, wherein, if $n = 1$, R_1 is phenyl which is unsubstituted or substituted in para-position by C_1 - C_{18} alkylthio or di(C_1 - C_4 alkyl)amino; mono- to penta-substituted alkylphenyl containing together a total of at most 18 carbon atoms in the 1 to 5 alkyl substituents; naphthyl, biphenyl, terphenyl, phenanthryl, anthryl, fluorenyl, carbazolyl, thienyl, pyrrolyl, phenothizinyll or 5,6,7,8-tetrahydronaphthyl, each of which is unsubstituted or substituted by C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_1 - C_4 alkylthio, hydroxy or amino.

Preference is given to compounds of the formula I in which, if n is 2,

10 R_1 is $-R_{12}-X-R_{13}-$,

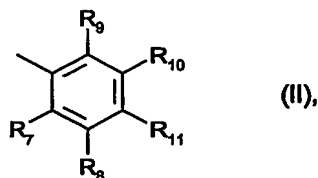
R_{12} and R_{13} are phenylene,

X is oxygen or $-NR_{31}-$, and

R_{31} is C_1 - C_4 alkyl.

15 Preference is also given to compounds of the formula I in which, if n is 1,

R_1 is unsubstituted or C_1 - C_4 alkyl-, C_1 - C_4 alkoxy-, C_1 - C_4 alkylthio-, hydroxyl-, halo-, amino-, C_1 - C_4 alkylamino- or di(C_1 - C_4 alkyl)amino-substituted naphthyl, phenanthryl, thienyl, dibenzofuryl, carbazolyl, fluorenyl or a radical of the formula II



- 20 R_7 , R_8 , R_9 , R_{10} and R_{11} independently of one another are hydrogen, chlorine, bromine, hydroxyl, C_1 - C_{18} alkyl, C_2 - C_{18} alkyl interrupted by oxygen or sulfur; C_1 - C_{18} alkoxy, C_2 - C_{18} alkoxy interrupted by oxygen or sulfur; C_1 - C_{18} alkylthio, C_3 - C_{12} alkenyloxy, C_3 - C_{12} alkynyloxy, C_7 - C_9 phenylalkyl, C_7 - C_9 phenylalkoxy, unsubstituted or C_1 - C_4 alkyl-substituted phenyl; phenoxy, cyclohexyl, C_5 - C_8 cycloalkoxy, C_1 - C_4 alkylamino, di(C_1 - C_4 alkyl)amino,
- 25 C_1 - C_{12} alkanoyl, C_3 - C_{12} alkanoyl interrupted by oxygen or sulfur; C_1 - C_{12} alkanoyloxy, C_3 - C_{12} alkanoyloxy interrupted by oxygen or sulfur; C_1 - C_{12} alkanoylamino, C_3 - C_{12} alkenoyl, C_3 - C_{12} alkenoyloxy, cyclohexylcarbonyl, cyclohexylcarbonyloxy, benzoyl or C_1 - C_4 alkyl-

substituted benzoyl; benzoyloxy or C_1 - C_4 alkyl-substituted benzoyloxy; $\text{---O---}\overset{\overset{R_{18}}{|}}{\underset{\underset{R_{19}}{|}}{C}}\text{---}\overset{\overset{O}{||}}{C}\text{---}R_{16}$



and R₁₁, together with the carbon atoms to which they are attached, form a benzo ring,



R₁₈ and R₁₉ independently of one another are hydrogen or C₁-C₄alkyl,

5 R_{20} is hydrogen,

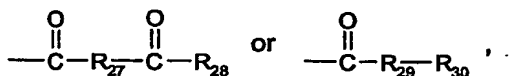
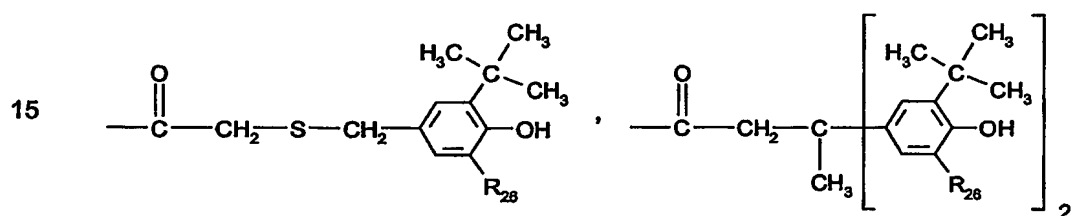
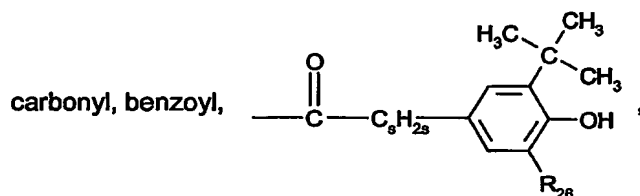
R₂₁ is hydrogen, phenyl, C₁-C₁₈alkyl, C₂-C₁₈alkyl interrupted by oxygen or sulfur;

C₇-C₈phenylalkyl, C₇-C₁₆-phenylalkyl which is unsubstituted or substituted on the phenyl radical from 1 to 3 times by C₁-C₄alkyl and is interrupted by oxygen or sulfur, or else the radicals R₂₀ and R₂₁, together with the carbon atoms to which they are attached, form a

10 cyclohexylene ring which is unsubstituted or substituted from 1 to 3 times by C₁-C₄alkyl,

R₂₂ is hydrogen or C₁-C₄alkyl,

R₂₃ is hydrogen, C₁-C₁₈alkanoyl, C₃-C₁₈alkenoyl, C₃-C₁₂alkanoyl interrupted by oxygen or sulfur; C₂-C₁₂alkanoyl substituted by a di(C₁-C₈alkyl)phosphonate group; C₆-C₉cycloalkyl-



R₂₄ and R₂₅ independently of one another are hydrogen or C₁-C₁₂alkyl,

R₂₆ is hydrogen or C₁-C₄alkyl,

- 20 -

R_{27} is C_1 - C_{12} alkylene, C_2 - C_8 alkenylene, C_2 - C_8 alkylidene, C_7 - C_{12} phenylalkylidene, C_5 - C_8 cycloalkylene or phenylene,

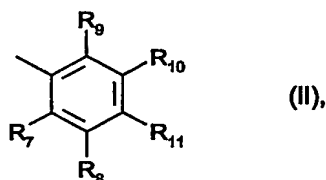
R_{28} is hydroxyl, C_1 - C_{12} alkoxy or $\text{---N} \begin{matrix} \nearrow R_{24} \\ \searrow R_{25} \end{matrix}$,

R_{29} is oxygen or -NH-,

- 5 R_{30} is C_1 - C_{18} alkyl or phenyl, and
s is 1 or 2.

Preference is likewise given to compounds of the formula I in which, if n is 1,

- 10 R_1 is phenanthryl, thienyl, dibenzofuryl, unsubstituted or C_1 - C_4 alkyl-substituted carbazolyl; or
is fluorenyl; or R_1 is a radical of the formula II



R_7 , R_8 , R_9 , R_{10} and R_{11} independently of one another are hydrogen, chlorine, hydroxyl, C_1 - C_{18} alkyl, C_1 - C_{18} alkoxy, C_1 - C_{18} alkylthio, C_3 - C_4 alkenyloxy, C_3 - C_4 alkynyloxy,

C_2 - C_{18} alkanoyloxy, phenyl, benzoyl, benzoyloxy or $\text{---O} \begin{matrix} | & R_{20} & R_{21} \\ \text{---C} & & \text{---C} & \text{---O---}R_{23} \\ | & & | \\ H & & R_{22} \end{matrix}$,

- 15 R_{20} is hydrogen,
 R_{21} is hydrogen, phenyl or C_1 - C_{18} alkyl, or else the radicals R_{20} and R_{21} , together with the
carbon atoms to which they are attached, form a cyclohexylene ring which is unsubstituted or
substituted from 1 to 3 times by C_1 - C_4 alkyl,
 R_{22} is hydrogen or C_1 - C_4 alkyl, and
20 R_{23} is hydrogen, C_1 - C_{18} alkanoyl or benzoyl.

Particular preference is given to compounds of the formula I in which, if n is 1,

R_7 , R_8 , R_9 , R_{10} and R_{11} independently of one another are hydrogen, C_1 - C_4 alkylthio or phenyl.

- 25 Of particular interest is a composition containing at least one compound of the formula I in
which

- 21 -

R₂, R₃, R₄ and R₅ independently of one another are hydrogen, chlorine, C₁-C₁₈alkyl, benzyl, phenyl, C₅-C₈cycloalkyl, C₁-C₁₈alkoxy, C₁-C₁₈alkylthio, C₁-C₁₈alkanoyloxy, C₁-C₁₈alkanoylamino, C₃-C₁₈alkenoyloxy or benzoyloxy; or else the radicals R₂ and R₃ or the radicals R₃ and R₄ or the radicals R₄ and R₅, together with the carbon atoms to which they are attached, form a benzo ring, R₄ is additionally -(CH₂)_p-COR₁₅ or -(CH₂)_qOH, or, if R₃, R₅ and R₆ are hydrogen, R₄ is additionally a radical of the formula III,

R₁₅ is hydroxyl, C₁-C₁₂alkoxy or $\text{---N} \begin{matrix} \text{R}_{24} \\ \text{R}_{25} \end{matrix}$,

R₁₆ and R₁₇ are methyl groups or, together with the C atom to which they are attached, form a C₅-C₈cycloalkylidene ring which is unsubstituted or substituted from 1 to 3 times by

C₁-C₄alkyl,

R₂₄ and R₂₅ independently of one another are hydrogen or C₁-C₁₂alkyl,

p is 1 or 2, and

q is 2, 3, 4, 5 or 6.

15. Also of particular interest is a composition containing at least one compound of the formula I in which at least two of the radicals R₂, R₃, R₄ and R₅ are hydrogen.

Of special interest is a composition containing at least one compound of the formula I in which R₃ and R₆ are hydrogen.

Of very special interest is composition containing at least one compound of the formula I in which

R₂ is C₁-C₄alkyl,

R₃ is hydrogen,

R₄ is C₁-C₄alkyl or, if R₆ is hydrogen, R₄ is additionally a radical of the formula III,

R₅ is hydrogen, and

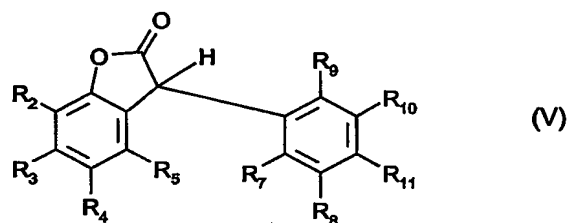
R₁₆ and R₁₇, together with the C atom to which they are attached, form a cyclohexylidene ring.

The following compounds are examples of the benzofuran-2-one type which are particularly suitable in the composition of the present invention: 3-[4-(2-acetoxyethoxy)phenyl]-5,7-di-tert-butyl-benzofuran-2-one; 5,7-di-tert-butyl-3-[4-(2-stearoyloxyethoxy)phenyl]benzofuran-2-one;

- 22 -

3,3'-bis[5,7-di-tert-butyl-3-(4-[2-hydroxyethoxy]phenyl)benzofuran-2-one]; 5,7-di-tert-butyl-3-(4-ethoxyphenyl)benzofuran-2-one; 3-(4-acetoxy-3,5-dimethylphenyl)-5,7-di-tert-butylbenzofuran-2-one; 3-(3,5-dimethyl-4-pivaloyloxy-phenyl)-5,7-di-tert-butylbenzofuran-2-one; 5,7-di-tert-butyl-3-phenylbenzofuran-2-one; 5,7-di-tert-butyl-3-(3,4-dimethylphenyl)-benzofuran-2-one; 5,7-di-tert-butyl-3-(2,3-dimethylphenyl)benzofuran-2-one.

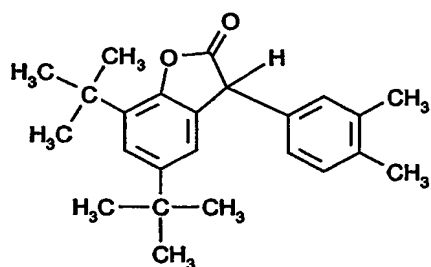
Also of special interest is a composition containing at least one compound of the formula V



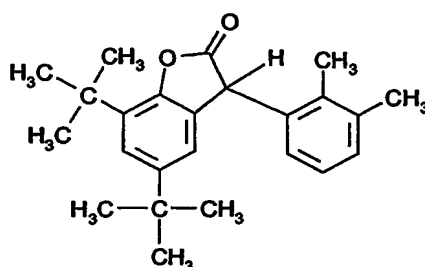
in which

- 10 R₂ is hydrogen or C₁-C₆alkyl,
 R₃ is hydrogen,
 R₄ is hydrogen or C₁-C₆alkyl,
 R₅ is hydrogen,
 R₇, R₈, R₉, R₁₀ and R₁₁ independently of one another are hydrogen, C₁-C₄alkyl or C₁-C₄alkoxy,
 15 with the proviso that at least two of the radicals R₇, R₈, R₉, R₁₀ or R₁₁ are hydrogen.

Very particular preference is given to a composition containing at least one compound of the formula Va or Vb



(Va)



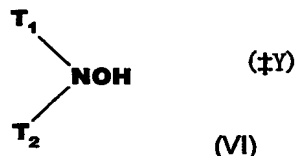
(Vb)

- 20 or a mixture of the two compounds of the formula Va and Vb.

- 23 -

Long chain N,N-dialkylhydroxylamine antioxidants useful in the composition of the present invention are those disclosed in U.S. Patent No. 4,876,300, which is incorporated herein by reference.

- 5 The long chain N,N-dialkylhydroxylamine antioxidants useful in the composition of the present invention include those of formula (VI)



- wherein T₁ and T₂ are independently alkyl of 6 to 36 carbon atoms, preferably 12-36 carbon atoms and most preferably 16-18 carbon atoms. Of particular interest is the long chain hydroxylamine for formula (VI) wherein T₁ and T₂ are the same and are a straight chain alkyl of 18 carbon atoms.

- The hydroxylamine antioxidants in the present compositions and methods are, for example, N,N-dioctylhydroxylamine, N,N-dilaurylhydroxylamine, N,N-didodecylhydroxylamine, N,N-ditetradecylhydroxylamine, N,N-dihexadecylhydroxylamine, N,N-dioctadecylhydroxylamine, N-hexadecyl-N-tetradecylhydroxylamine, N-hexadecyl-N-heptadecylhydroxylamine, N-hexadecyl-N-octadecylhydroxylamine, N-heptadecyl-N-octadecylhydroxylamine, N-methyl-N-octadecylhydroxylamine and N,N-di(hydrogenated tallow)hydroxylamine. Compounds of special interest are those where T₁ and T₂ are each dodecyl, tetradecyl, hexadecyl or octadecyl; or where T₁ is hexadecyl and T₂ is tetradecyl, heptadecyl or octadecyl; or where T₁ is heptadecyl and T₂ is octadecyl.

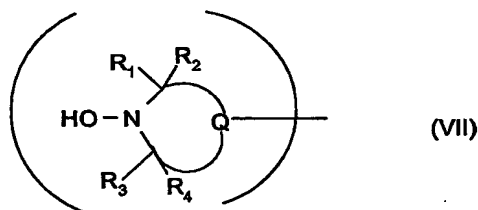
- The long chain hydroxylamine antioxidant in the present invention may be for example the N,N-di(alkyl)hydroxylamine produced by the direct oxidation of N,N-di(hydrogenated tallow)amine (Irgastab® FS-042, Ciba Specialty Chemicals Corp.).

- The substituted hydroxylamine antioxidants of the present invention are for example those described in U.S. Pat. Nos. 4,666,962, 4,666,963, 4,678,826, 4,753,972, 4,757,102, 4,760,179, 4,929,657, 5,057,563, 5,021,479, 5,045,583 and 5,185,448 the disclosures of which are hereby incorporated by reference. These include the Michael addition products from the reaction of the hydroxylamines of formula VI with any α,β-unsaturated ketone, ester, amide, or phosphonate; and also includes Mannich-type condensation products from the

- 24 -

reaction of the hydroxylamines of formula VI with formaldehyde and secondary amines. Also included are O-alkenyl substituted analogues of the hydroxylamines as disclosed in U.S. Pat. No. 5,045,583. also includes non-hindered substituted hydroxylamines as disclosed in U.S. Pat. No. 5,185,448 and acyl derivatives of the unsubstituted hydroxylamine antioxidants for example such as those disclosed in U.S. Pat. No. 5,021,479.

The substituted hydroxylamines may be derivatives of the above-described hydroxylamines of formulae (VI) or hydroxylamines of the formula (VII)

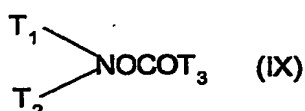


wherein

Q is a group forming a five- or six-membered ring; and

R₁, R₂, R₃ and R₄ are independently hydrogen, alkyl of 1 to 4 carbon atoms or phenyl, provided that if they are derivatives of hydroxylamines of formula (VII), that they are limited to derivatives of hydroxylamines as described in U.S. Pat. Nos. 5,185,448 and 5,235,056.

The present substituted hydroxylamines may be for example of the formula (VIII) or (IX)



wherein

T₁ is straight or branched chain alkyl of 1 to 36 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, aralkyl of 7 to 9 carbon atoms, or said aralkyl substituted by one or two alkyl of 1 to 12 carbon atoms or by one or two halogen atoms;

T₂ is hydrogen, or independently has the same meaning as T₁; and

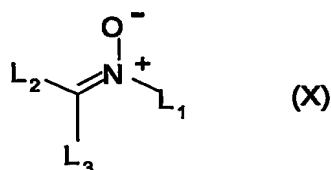
T₃ is allyl, straight or branched chain alkyl of 1 to 36 carbon atoms, cycloalkyl of 5 to 18 carbon atoms, cycloalkenyl of 5 to 18 carbon atoms or a straight or branched chain alkyl of 1 to 4 carbon atoms substituted by phenyl or by phenyl substituted by one or two alkyl groups of 1 to 4 carbon atoms or by 1 or 2 halogen atoms.

- 25 -

The substituted hydroxylamines may be for example O-allyl-N,N-dioctadecylhydroxylamine or O-n-propyl-N,N-dioctadecylhydroxylamine or N,N-di(hydrogenated tallow)acetoxamine.

5 The nitrones may be for example as described in U.S. Pat. No. 4,898,901, which is hereby incorporated by reference.

The nitrones of are for example of the formula (X)



wherein

10 L₁ is straight or branched chain alkyl of 1 to 36 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, aralkyl of 7 to 9 carbon atoms, or said aralkyl substituted by one or two alkyl of 1 to 12 carbon atoms or by one or two halogen atoms;

15 L₂ and L₃ are independently hydrogen, straight or branched chain alkyl of 1 to 36 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, aralkyl of 7 to 9 carbon atoms, or said aralkyl substituted by one or two alkyl of 1 to 12 carbon atoms or by one or two halogen atoms;

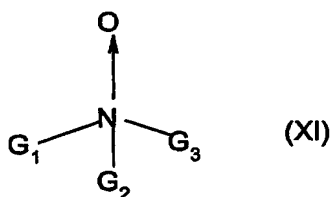
or L₁ and L₂ together form a five- or six-membered ring including the nitrogen atom.

20 The nitrones of may be the corresponding oxidation products of the unsubstituted hydroxylamines. That is to say, the nitrones may be nitron analogues of the unsubstituted hydroxylamines. The nitrones may be for example, N-benzyl- α -phenylnitron, N-ethyl- α -methylnitron, N-octyl- α -heptylnitron, N-lauryl- α -undecylnitron, N-tetradecyl- α -tridcylnitron, N-hexadecyl- α -pentadecylnitron, N-octadecyl- α -heptadecylnitron, N-hexadecyl- α -heptadecylnitron, N-octadecyl- α -pentadecylnitron, N-heptadecyl- α -heptadecylnitron, N-octadecyl- α -hexadecylnitron, N-methyl- α -heptadecylnitron and the
25 nitron derived from N,N-di(hydrogenated tallow)hydroxylamine.

- 26 -

The amine oxides of are for example those disclosed in U.S. Pat. Nos. 5,081,300, 5,162,408, 5,844,029, 5,880,191 and 5,922,794, the relevant parts of each incorporated herein by reference.

- 5 The amine oxides are for example saturated tertiary amine oxides as represented by general formula (XI):



wherein

- 10 G_1 and G_2 are independently a straight or branched chain alkyl of 6 to 36 carbon atoms, aryl of 6 to 12 carbon atoms, aralkyl of 7 to 36 carbon atoms, alkaryl of 7 to 36 carbon atoms, cycloalkyl of 5 to 36 carbon atoms, alkylcycloalkyl of 6 to 36 carbon atoms or cycloalkylalkyl of 6 to 36 carbon atoms;

- 15 G_3 is a straight or branched chain alkyl of 1 to 36 carbon atoms, aryl of 6 to 12 carbon atoms, aralkyl of 7 to 36 carbon atoms, alkaryl of 7 to 36 carbon atoms, cycloalkyl of 5 to 36 carbon atoms, alkylcycloalkyl of 6 to 36 carbon atoms or cycloalkylalkyl of 6 to 36 carbon atoms; with the proviso that at least one of G_1, G_2 and G_3 contains a b carbon-hydrogen bond; and

- wherein said aryl groups may be substituted by one to three halogen, alkyl of 1 to 8 carbon atoms, alkoxy of 1 to 8 carbon atoms or combinations thereof; and

- 20 wherein said alkyl, aralkyl, alkaryl, cycloalkyl, alkylcycloalkyl and cycloalkylalkyl groups may be interrupted by one to sixteen -O-, -S-, -SO-, -SO₂-, -COO-, -OCO-, -CO-, -NG₄-, -CONG₄- and -NG₄CO- groups, or wherein said alkyl, aralkyl, alkaryl, cycloalkyl, alkylcycloalkyl and cycloalkylalkyl groups may be substituted by one to sixteen groups selected from -OG₄, -SG₄, -COOG₄, -OCOG₄, -COG₄, -N(G₄)₂, -CON(G₄)₂, -NG₄COG₄ and 5- and 6-membered rings containing the -C(CH₃)(CH₂R_x)NL(CH₂R_x)(CH₃)C- group or wherein said alkyl, aralkyl, alkaryl, cycloalkyl, alkylcycloalkyl and cycloalkylalkyl groups are both interrupted and substituted by the groups mentioned above; and

wherein

- 30 G_4 is independently hydrogen or alkyl of 1 to 8 carbon atoms;
 R_x is hydrogen or methyl;

- 27 -

L is hydrogen, hydroxy, C₁₋₃₀ straight or branched chain alkyl moiety, a -C(O)R moiety where R is a C₁₋₃₀ straight or branched chain alkyl group, or a -OR_y moiety; and

R_y is C₁₋₃₀ straight or branched chain alkyl, C₂-C₃₀ alkenyl, C₂-C₃₀ alkynyl, C₅-C₁₂ cycloalkyl, C₆-C₁₀ bicycloalkyl, C₅-C₈ cycloalkenyl, C₆-C₁₀ aryl, C₇-C₉ aralkyl, C₇-C₉ aralkyl
 5 substituted by alkyl or aryl, or -CO(D), where D is C₁-C₁₈ alkyl, C₁-C₁₈ alkoxy, phenyl, phenyl substituted by hydroxy, alkyl or alkoxy, or amino or amino mono- or di-substituted by alkyl or phenyl.

Examples of structures of formula (XI) are where G₁ and G₂ are independently benzyl or
 10 substituted benzyl. It is also possible for each of G₁, G₂, and G₃ to be the same residue. G₁ and G₂ may also independently be alkyl groups of 8 to 26 carbon atoms, for example alkyl groups of 10 to 26 carbon atoms. G₃ may be an alkyl group of 1 to 22 carbon atoms, for example methyl or substituted methyl. Also, the present amine oxides include those wherein
 15 residues for G₁, G₂, and G₃ are, for instance, saturated hydrocarbon residues or saturated hydrocarbon residues containing at least one of the aforementioned -O-, -S-, -SO-, -CO₂-, -CO-, or -CON- moieties. Those skilled in the art will be able to envision other useful residues for each of G₁, G₂, and G₃ without detracting from the present invention.

20 The saturated amine oxides may also includes poly(amine oxides). By poly(amine oxides) is meant tertiary amine oxides containing at least two tertiary amine oxides per molecule. Illustrative poly(amine oxides), also called "poly(tertiary amine oxides)", include the tertiary amine oxide analogues of aliphatic and alicyclic diamines such as, for example, 1,4-diaminobutane; 1,6-diaminohexane; 1,10-diaminodecane; and 1,4-diaminocyclohexane,
 25 and aromatic based diamines such as, for example, diamino anthraquinones and diaminoanisoles.

Also included are tertiary amine oxides derived from oligomers and polymers of the aforementioned diamines. Useful amine oxides also include amine oxides attached to
 30 polymers, for example, polyolefins, polyacrylates, polyesters, polyamides, polystyrenes, and the like. When the amine oxide is attached to a polymer, the average number of amine oxides per polymer can vary widely as not all polymer chains need to contain an amine oxide. All of the aforementioned amine oxides may optionally contain at least one -O-, -S-,

- 28 -

-SO-, -CO₂-, -CO-, or -CONG₄- moiety. For instance, each tertiary amine oxide of the polymeric tertiary amine oxide may contain a C₁ residue.

Specific examples of preferred antioxidants of the present invention are one or more
5 compounds selected from

i.) an N,N-di(alkyl)hydroxylamine produced by the direct oxidation of N,N-di(hydrogenated tallow)amine (Irgastab[®] FS-042),

10 ii.) O-allyl-N,N-dioctadecylhydroxylamine,

iii.) N-octadecyl-a-heptadecylnitrone, and

15 iv.) a di(C₁₆-C₁₈)alkyl methyl amine oxide, (Genox[™] EP).

Irgastab[®] FS-042 is available from Ciba Specialty Chemicals. Genox[™] EP is available from GE Specialty Chemicals. O-allyl-N,N-dioctadecylhydroxylamine is as prepared in Example 3 of U.S. Pat. No. 5,045,583. N-octadecyl-a-heptadecylnitrone is as prepared in Example 3 of U.S. Pat. No. 4,898,901.

20

The antioxidants of this invention are provided in compositions of this invention in a minor amount based on the weight of the edible organic substance, which amount is effective as an antioxidant, i.e. sufficient to stabilize, or retard the deterioration of, the edible organic substances to be stored and used to prepare foods in a normal and acceptable manner. The
25 amount of antioxidant employed is generally any amount which may have a significant stabilizing effect. The amount of the compounds of this invention present may depend on the desired period of stability of the edible organic substance and the rate of deterioration of the edible organic substance. Thus, increased amounts of the compound of the present invention may be employed when an increased storage life of the edible organic substance
30 before use is desired. Frequently, the compounds of the present invention will be provided in an amount of at least about 0.005%, preferably at least about 0.01%, by weight based on the weight of the edible organic substance up to a maximum of 5%, preferably up to about 1%. Concentrations of about 0.1 or more weight percent of the compounds of the present invention based on the edible organic substance are frequently employed in accordance with

- 29 -

the invention. At concentrations in excess of about 5% by weight based on the weight of the edible organic substance, little benefit in increased stability is generally observed.

The presence of the compounds of the present invention usually does not materially affect the manner in which the edible organic substance is formulated or in which it is used to prepare foods. The compounds of the present invention are preferably uniformly admixed in the edible organic substance. The compounds of the present invention may be added at the time of food preparation or may be intimately premixed with the edible fat or fatty oils to stabilize them prior to food preparation.

It is often convenient to provide an edible fat or fatty oil composition in which the volume of the product can easily be handled, particularly when the composition must be transported for its use in food preparation. On the other hand, this invention is applicable to large food processing plants where large volumes of edible organic substance are stored and used in food preparation. The compounds of the present invention, due to their low toxicity and low concentrations which can be effectively employed, are especially suitable for stabilization of large volume doughs such as pastry, cake and biscuit premix such as are used in the baking industry. Also, use in other large scale food production plants such as pet food and other animal feeds are other applications where the compounds of the present invention are especially suitable.

A combination of antioxidants is frequently used in edible fats and fatty oils and foods containing them. The compounds of the present invention may be utilized in conjunction with other food antioxidants to obtain desirable combinations of properties of stability and carry-through. The other food antioxidants can be used in an amount of from about 0.01-0.1% by weight based on the weight of the edible organic substance. They may also be combined with other food additives such as emulsifiers, suspension agents and colorings to provide the desired qualities in the final food product. Examples of such additional food antioxidants include the following:

1. Phenolics such as BHA and BHT.

2. Tocopherols, for example α -tocopherol, β -tocopherol, γ -tocopherol, δ -tocopherol and mixtures thereof (Vitamin E).

- 30 -

3. Benzylphosphonates, for example dimethyl-2,5-di-tert-butyl-4-hydroxybenzylphosphonate, diethyl-3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl-3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl-5-tert-butyl-4-hydroxy-3-methylbenzylphosphonate, the calcium salt of the monoethyl ester of 3,5-di-tert-butyl-4-hydroxybenzylphosphonic acid.

4. Esters of b-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, n-octanol, i-octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

5. Esters of b-(5-tert-butyl-4-hydroxy-3-methylphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, n-octanol, i-octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

6. Esters of b-(3,5-dicyclohexyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl)isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

7. Esters of 3,5-di-tert-butyl-4-hydroxyphenyl acetic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl)isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

- 31 -

8. Ascorbic acid (vitamin C)

9. Phosphites and phosphonites, for example triphenyl phosphite, diphenyl alkyl phosphites, phenyl dialkyl phosphites, tris(nonylphenyl) phosphite, trilauryl phosphite, trioctadecyl phosphite, dialkylpentaerythritol diphosphites, distearyl pentaerythritol diphosphite, tris(2,4-di-tert-butylphenyl) phosphite, diisodecyl pentaerythritol diphosphite, bis(2,4-di-tert-butylphenyl) pentaerythritol diphosphite (Ultranox® 626, GE Chemicals, formula (D)), bis(2,6-di-tert-butyl-4-methylphenyl)-pentaerythritol diphosphite, diisodecylpentaerythritol diphosphite, bis(2,4-di-tert-butyl-6-methylphenyl)pentaerythritol diphosphite, bis(2,4,6-tris(tert-butylphenyl)pentaerythritol diphosphite, tristearyl sorbitol triphosphite, tetrakis(2,4-di-tert-butylphenyl) 4,4'-biphenylene diphosponite (Irgafos® P-EPQ, Ciba Specialty Chemicals Corp., formula (H)), 6-isooctyloxy-2,4,8,10-tetra-tert-butyl-dibenzo[d,f][1,3,2]dioxaphosphopin, 6-fluoro-2,4,8,10-tetra-tert-butyl-12-methyl-dibenzo[d,g][1,3,2]dioxaphosphocin, bis(2,4-di-tert-butyl-6-methylphenyl) methyl phosphite, bis(2,4-di-tert-butyl-6-methylphenyl) ethyl phosphite, 2,2',2''-nitrilo[triethyltris(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl)phosphite], 2-ethylhexyl(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl)phosphite.

10. Rosemary Extract

The following examples are for illustrative purposes only and are not to be construed to limit the scope of the instant invention in any manner whatsoever.

Experimental Methods.

Corn oil (3g) stripped of natural tocopherols was oxidized in stoppered 50ml Erlenmeyer flasks in a shaker oven (Lab-Line Instrument, Inc, Melrose Park, IL). Lipid oxidation was followed by measuring peroxide values colorimetrically, and hexanal by static headspace gas chromatography. Periodic values were determined by the ferric thiocyanate method (Chapman, R.A.; Mackay, K. The estimation of peroxides in fats and oils by the ferric thiocyanate method. J. Am. Oil Chem. Soc. 1949, 26, 360-363), modified for safety reasons using choloform: methanol (3:1, v/v) instead of benzene:methanol as solvent. Propanol was determined by static headspace gas chromatography (Frankel, E.N. Formation of headspace volatiles by thermal decomposition of oxidized fish oils vs. oxidized vegetable oils. J. Am. Oil.

- 32 -

Chem. Soc. 1993, 70, 767-772). Aliquots of oil samples (0.20 g) were weighed into 22-ml headspace vials, sealed and equilibrated at 80° C for 10 min in an HS-40 headspace autosampler. An aliquot of the headspace was then injected in an autosystem gas chromatograph (Perkin-Elmer, Norwalk, CT) equipped with a capillary DB-1701 column, 30 m long, 0.32 mm id, and 1 µm film thickness (J&W Scientific, Folsom, CA). The injector and detector temperatures were 180 and 200°C, respectively. The oven temperature was controlled isothermally at 65°C. Hexanal was quantified by using standard solutions of known concentrations. All analyses were carried out in duplicate.

- 10 The activity of the antioxidants was evaluated by determining peroxide values and hexanal using corn oil stripped of natural tocopherols after oxidation at 50 and 60°C. Peroxide values measurements are classical measurements of hydroperoxides that are generally accepted in antioxidant evaluations. This measure is useful at relatively low levels of oxidation and the temperatures used in this study which are sufficiently mild so that hydroperoxides are not
- 15 markedly decomposed. Hexanal determinations are measurements of hydroperoxide decomposition which may be more closely related to flavor deterioration and rancidity than peroxide values. Antioxidants in accordance with the present invention that were tested were (1) 042 - an N,N-di(alkyl)hydroxylamine produced by the direct oxidation of N,N-di(hydrogenated tallow)amine (commercially available from Ciba Specialty Chemicals
- 20 Corporation Irgastab® FS-042) and Irganox® HP-136 – 3-(3,4-dimethylphenyl)-5,7-di-tert-butyl-benzofuran-2-one. The antioxidants were tested at 100 and 200 ppm and compared with the commercial antioxidants BHA, BHT and TBHQ and commercial natural antioxidants tocopherol mixtures at the same concentration and a rosemary extract at 250 and 500 ppm.
- 25 For the evaluations at 50°C, an endpoint was selected of 8 days for both peroxide values and hexanal contents during the propagation stage where the rate of oxidation is accelerated. The results of the evaluations are shown in Tables 1-2.

- For the evaluations at 60°C, an endpoint was selected of 3 days for peroxide values and 4
- 30 days for hexanal contents during the propagation stage where the rate of oxidation is accelerated. The results of the evaluations are shown in Tables 3-4.

- 33 -

Table 1

Oil samples	Peroxide value (meq/kg)				Hexanal (x1000 mmol/kg)		
	Day 2	Day 4	Day 8	Day 10	Day 4	Day 8	Day 10
BHA 100 ppm	9.2	21.0	55.5	77.0	18.0	18.3	16.3
BHA 200 ppm	9.7	21.2	53.5	72.2	16.2	17.1	21.1
BHT 100 ppm	7.5	16.8	43.5	62.2	13.2	22.9	20.2
BHT 200 ppm	4.8	10.3	3.3	32.4	8.6	17.2	15.1
TBHQ 100 ppm	0.7	0.7	1.6	2.3	7.7	8.7	7.0
TBHQ 200 ppm	0.5	1.2	1.6	2.1	7.5	11.7	17.8
Tocopherols 100 ppm	10.1	24.4	58.7	84.1	12.1	40.0	75.9
Tocopherols 200 ppm	13.5	28.1	79.9	101.9	16.5	19.6	75.3
Rosemary 250 ppm	2.2	4.2	8.5	10.7	9.5	29.3	53.6
Rosemary 500 ppm	2.0	4.1	7.7	10.4	7.0	143.4	286.6
Irgastab® FS-042 100 ppm	1.0	1.9	4.1	14.3	4.3	76.4	110.0
Irgastab® FS-042 200 ppm	1.0	1.7	3.5	8.0	3.9	13.7	21.0
Irganox® HP-136 100 ppm	1.9	6.1	20.2	47.1	6.0	37.9	210.8
Irganox® HP-136 200 ppm	2.4	5.1	16.4	86.1	14.5	14.5	97.3

- 34 -

Table 2

Oil samples	Inhibition of Peroxide Values (%)				Inhibition of Hexanal (%)		
	Day 2	Day 4	Day 8	Day 10	Day 4	Day 8	Day 10
BHA 100 ppm	1.3	6.8	20.4	31.6	-29.4	77.2	94.3
BHA 200 ppm	-6.1	-0.6	22.0	29.6	26.2	78.8	81.9
BHT 100 ppm	19.0	25.6	37.7	44.7	5.4	71.4	93.0
BHT 200 ppm	47.6	51.1	95.2	68.4	60.9	78.7	87.1
TBHQ 100 ppm	92.1	97.0	97.7	98.0	44.5	89.2	97.6
TBHQ 200 ppm	94.8	94.4	97.6	97.9	65.9	85.5	84.7
Tocopherols 100 ppm	-8.2	-8.1	15.8	25.2	13.2	50.1	73.7
Tocopherols 200 ppm	-47.7	-33.0	-16.5	0.6	25.1	75.7	35.5
Rosemary 250 ppm	76.4	79.9	87.6	89.5	56.7	63.7	54.0
Rosemary 500 ppm	78.7	82.0	89.0	90.8	49.9	-78.9	0.6
Irgastab® FS-042 100 ppm	89.3	91.6	94.1	51.0	65.8	38.9	61.1
Irgastab® FS-042 200 ppm	89.0	91.9	94.9	92.2	69.0	89.1	81.0
Irganox® HP-136 100 ppm	79.1	73.1	71.0	58.2	56.8	52.8	26.9
Irganox® HP-136 200 ppm	74.2	75.9	76.2	16.0	33.9	82.0	16.6

- 35 -

Table 3

Oil samples	Peroxide value (meq/kg)				Hexanal (x1000 mmol/kg)		
	Day 1	Day 2	Day 3	Day 4	Day 2	Day 3	Day 4
BHA 100 ppm	9.6	25.6	52.0	84.6	21.5	32.8	54.6
BHA 200 ppm	7.9	20.4	38.1	61.2	18.9	18.3	30.2
BHT 100 ppm	5.9	14.8	26.6	45.1	11.6	14.8	82.6
BHT 200 ppm	4.7	11.7	21.6	33.2	14.1	15.4	12.7
TBHQ 100 ppm	0.4	1.2	1.2	1.7	7.9	7.7	16.0
TBHQ 200 ppm	0.0	0.2	0.9	1.1	7.5	10.1	12.4
Tocopherols 100 ppm	9.4	22.9	40.1	55.1	13.9	21.8	238.8
Tocopherols 200 ppm	9.2	22.9	40.8	58.0	13.8	14.8	17.8
Rosemary 250 ppm	1.2	3.1	5.5	7.8	11.5	26.3	120.3
Rosemary 500 ppm	1.7	3.5	4.8	6.9	7.6	12.4	19.9
Irgastab® FS-042 100 ppm	1.5	2.2	2.7	3.2	7.5	4.2	5.9
Irgastab® FS-042 200 ppm	0.7	1.6	2.4	4.0	12.6	20.9	34.4
Irganox® HP-136 100 ppm	6.1	5.3	9.5	216.4	8.9	10.3	9.5
Irganox® HP-136 200 ppm	6.0	4.1	7.4	51.6	13.0	33.6	141.7

- 36 -

Table 4

Oil samples	Inhibition of Peroxide Values (%)				Inhibition of Hexanal (%)		
	Day 1	Day 2	Day 3	Day 4	Day 2	Day 3	Day 4
BHA 100 ppm	-15.7	-13.0	-11.1	4.6	-29.3	18.3	72.8
BHA 200 ppm	11.2	18.9	36.7	42.6	45.3	82.3	81.9
BHT 100 ppm	29.5	34.6	43.3	48.9	30.9	62.0	67.0
BHT 200 ppm	47.0	53.9	64.3	68.8	53.2	84.2	96.1
TBHQ 100 ppm	94.8	94.8	97.4	98.1	51.6	79.0	90.3
TBHQ 200 ppm	103.3	99.2	98.4	99.0	73.6	91.8	96.7
Tocopherols 100 ppm	-12.2	-1.0	14.5	37.1	16.6	45.8	-45.2
Tocopherols 200 ppm	-6.0	7.7	31.8	45.5	56.0	85.5	94.5
Rosemary 250 ppm	86.2	87.5	90.8	92.7	62.0	69.2	47.4
Rosemary 500 ppm	79.3	84.7	89.8	92.1	54.1	65.2	87.9
Irgastab® FS-042 100 ppm	82.3	90.3	94.2	96.5	57.7	91.7	98.1
Irgastab® FS-042 200 ppm	93.2	94.0	96.2	96.3	44.2	71.2	84.4
Irganox® HP-136 100 ppm	26.4	76.5	79.5	-135.5	49.9	79.4	97.0
Irganox® HP-136 200 ppm	40.5	85.0	88.2	52.3	42.4	53.6	35.9